### **PCT**

# WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



#### INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6:
C11D 1/94, 1/86, 1/65, 1/825, 1/83, 17/00
A1
(43) International Publication Number: 12 November 1998 (12.11.98)

(21) International Application Number: PCT/US98/08754 (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ,

(30) Priority Data:

08/853,358

8 May 1997 (08.05.97)

US

(71) Applicant: COLGATE-PALMOLIVE COMPANY [US/US]; 300 Park Avenue, New York, NY 10022 (US).

(72) Inventors: DURBUT, Patrick; 25, avenue des Villas, B-4800 Verviers (BE). BROZE, Guy; 32, rue Claskin, B-4460 Grace-Hollogne (BE).

(74) Agent: NANFELDT, Richard, E.; Colgate-Palmolive Company, 909 River Road, Piscataway, NJ 08855-1343 (US).

BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

#### **Published**

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: CLEANING COMPOSITIONS

#### (57) Abstract

The present invention relates to a cleaning composition containing at least one first surfactant selected from the group consisting of nonionic surfactants, anionic surfactants, partially esterified ethoxylated glycerol surfactants, and alkyl polyglucoside surfactants and mixtures thereof and a second surfactant selected from the group consisting of sulfonamide, hydroxy sulfobetaine, betaines, amine oxides, glucoamides,  $N-C_{1-3}$  alkyl  $C_8-C_{16}$  alkyl glucoamide, and  $C_5-C_{12}$  N-alkyl aldoamide and mixtures thereof and water.

### FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

$\mathbf{AL}$	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
$\mathbf{AM}$	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
ВJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	$\mathbf{UZ}$	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	$\mathbf{z}\mathbf{w}$	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
$\mathbf{cz}$	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

WO 98/50508 PCT/US98/08754

#### **CLEANING COMPOSITIONS**

#### Background of the Invention

5

10

15

20

25

In recent years all-purpose liquid detergents have become widely accepted for cleaning hard surfaces, e.g., painted woodwork and panels, tiled walls, wash bowls, bathtubs, linoleum or tile floors, washable wall paper, etc. Such all-purpose liquids comprise clear and opaque aqueous mixtures of water-soluble synthetic organic detergents and water-soluble detergent builder salts. In order to achieve comparable cleaning efficiency with granular or powdered all-purpose cleaning compositions, use of water-soluble inorganic phosphate builder salts was favored in the prior art all-purpose liquids. For example, such early phosphate-containing compositions are described in U.S. Patent Nos. 2,560,839; 3,234,138; 3,350,319; and British Patent No. 1,223,739.

In view of the environmentalist's efforts to reduce phosphate levels in ground water, improved all-purpose liquids containing reduced concentrations of inorganic phosphate builder salts or non-phosphate builder salts have appeared. A particularly useful self-opacified liquid of the latter type is described in U.S. Patent No. 4,244,840.

However, these prior art all-purpose liquid detergents containing detergent builder salts or other equivalent tend to leave films, spots or streaks on cleaned unrinsed surfaces, particularly shiny surfaces. Thus, such liquids require thorough rinsing of the cleaned surfaces which is a time-consuming chore for the user.

In order to overcome the foregoing disadvantage of the prior art all-purpose liquid, U.S. Patent No. 4,017,409 teaches that a mixture of paraffin sulfonate and a reduced concentration of inorganic phosphate builder salt should be employed. However, such compositions are not completely acceptable from an environmental point of view based upon the phosphate content. On the other hand, another alternative to achieving phosphate-free all-purpose liquids has been to use a major proportion of a mixture of anionic and nonionic detergents with minor amounts of glycol ether solvent and organic amine as shown in U.S. Patent NO. 3,935,130. Again, this approach has not been completely satisfactory and the high levels of organic detergents necessary to achieve

WO 98/50508 PCT/US98/08754

2

cleaning cause foaming which, in turn, leads to the need for thorough rinsing which has been found to be undesirable to today's consumers.

Another approach to formulating hard surfaced or all-purpose liquid detergent composition where product homogeneity and clarity are important considerations involves the formation of oil-in-water (o/w) microemulsions which contain one or more surface-active detergent compounds, a water-immiscible solvent (typically a hydrocarbon solvent), water and a "cosurfactant" compound which provides product stability. By definition, an o/w microemulsion is a spontaneously forming colloidal dispersion of "oil" phase particles having a particle size in the range of 25 Å to 800 Å in a continuous aqueous phase.

5

10

15

20

25

In view of the extremely fine particle size of the dispersed oil phase particles, microemulsions are transparent to light and are clear and usually highly stable against phase separation.

Patent disclosures relating to use of grease-removal solvents in o/w microemulsions include, for example, European Patent Applications EP 0137615 and EP 0137616 - Herbots et al; European Patent Application EP 0160762 - Johnston et al; and U.S. Patent No. 4,561,991 - Herbots et al. Each of these patent disclosures also teaches using at least 5% by weight of grease-removal solvent.

It also is known from British Patent Application GB 2144763A to Herbots et al, published March 13, 1985, that magnesium salts enhance grease-removal performance of organic grease-removal solvents, such as the terpenes, in o/w microemulsion liquid detergent compositions. The compositions of this invention described by Herbots et al. require at least 5% of the mixture of grease-removal solvent and magnesium salt and preferably at least 5% of solvent (which may be a mixture of water-immiscible non-polar solvent with a sparingly soluble slightly polar solvent) and at least 0.1% magnesium salt.

However, since the amount of water immiscible and sparingly soluble components which can be present in an o/w microemulsion, with low total active ingredients without impairing the stability of the microemulsion is rather limited (for example, up to 18% by weight of the aqueous phase), the presence of such high quantities of grease-removal

10

15

20

25

solvent tend to reduce the total amount of greasy or oily soils which can be taken up by and into the microemulsion without causing phase separation.

The following representative prior art patents also relate to liquid detergent cleaning compositions in the form of o/w microemulsions: U.S. Patents Nos.. 4,472,291 - Rosario; 4,540,448 - Gauteer et al; 3,723,330 - Sheflin; etc.

Liquid detergent compositions which include terpenes, such as d-limonene, or other grease-removal solvent, although not disclosed to be in the form of o/w microemulsions, are the subject matter of the following representative patent documents: European Patent Application 0080749; British Patent Specification 1,603,047; 4,414,128; and 4,540,505. For example, U.S. Patent No. 4,414,128 broadly discloses an aqueous liquid detergent composition characterized by, by weight:

- (a) from 1% to 20% of a synthetic anionic, nonionic, amphoteric or zwitterionic surfactant or mixture thereof;
- (b) from 0.5% to 10% of a mono- or sesquiterpene or mixture thereof, at a weight ratio of (a):(b) lying in the range of 5:1 to 1:3; and
- (c) from 0.5% 10% of a polar solvent having a solubility in water at 15°C in the range of from 0.2% to 10%. Other ingredients present in the formulations disclosed in this patent include from 0.05% to 2% by weight of an alkali metal, ammonium or alkanolammonium soap of a C13-C24 fatty acid; a calcium sequestrant from 0.5% to 13% by weight; non-aqueous solvent, e.g., alcohols and glycol ethers, up to 10% by weight; and hydrotropes, e.g., urea, ethanolamines, salts of lower alkylaryl sulfonates, up to 10% by weight. All of the formulations shown in the Examples of this patent include relatively large amounts of detergent builder salts which are detrimental to surface shine.
- U.S. Patent 5,082,584 discloses a microemulsion composition having an anionic surfactant, a cosurfactant, nonionic surfactant, perfume and water; however, these compositions do not possess the low ecotoxicity profile and the improved interfacial tension properties as exhibited by the compositions of the instant invention.

British Patent No 1,453,385 discloses polyesterified nonionic surfactants similar to the polyesterified nonionic surfactants of the instant invention. However, these nonionic

10

15

20

25

surfactants of British Patent 1,453,385 do not disclose the formula (II) portion of the instant composition. Additionally, the formulated compositions of British Patent 1,453,385 fail to disclose the critical limitations of the instant invention.

A number of patents teach esterified ethoxylated glycerol compounds for various applications. These patents are Great Britain 1,453,385; Japan 59-1600 and Japan 58-206693 and European Patent Application 0586,323A1. These publications fail to appreciate that a mixture of esterified ethoxylated glycerol and nonesterified ethoxylated glycerol, when used in a hard surface cleaning composition, functions as a grease release agent.

Nonionic surfactants are in general chemically inert and stable toward pH change and are therefore well suited for mixing and formulation with other materials. The superior performance of nonionic surfactants on the removal of oily soil is well recognized. Nonionic surfactants are also known to be mild to human skin. However, as a class, nonionic surfactants are known to be low or moderate foamers. Consequently, for detergents which require copious and stable foam, the application of nonionic surfactants is limited. There have been substantial interest and efforts to develop a high foaming detergent with nonionic surfactants as the major ingredient. Yet, little has been achieved.

The prior art is replete with light duty liquid detergent compositions containing nonionic surfactants in combination with anionic and/or betaine surfactants wherein the nonionic detergent is not the major active surfactant, as shown in U.S. Patent No. 3,658,985 wherein an anionic based shampoo contains a minor amount of a fatty acid alkanolamide. U.S. Patent No. 3,769,398 discloses a betaine-based shampoo containing minor amounts of nonionic surfactants. This patent states that the low foaming properties of nonionic detergents renders its use in shampoo compositions non-preferred. U.S. Patent No. 4,329,335 also discloses a shampoo containing a betaine surfactant as the major ingredient and minor amounts of a nonionic surfactant and of a fatty acid mono- or di-ethanolamide. U.S. Patent No. 4,259,204 discloses a shampoo comprising 0.8-20% by weight of an anionic phosphoric acid ester and one additional surfactant which may be either anionic, amphoteric, or nonionic. U.S. Patent No. 4,329,334 discloses an anionic-

10

15

20

25

amphoteric based shampoo containing a major amount of anionic surfactant and lesser amounts of a betaine and nonionic surfactants.

5

PCT/US98/08754

- U.S. Patent No. 3,935,129 discloses a liquid cleaning composition based on the alkali metal silicate content and containing five basic ingredients, namely, urea, glycerin, triethanolamine, an anionic detergent and a nonionic detergent. The silicate content determines the amount of anionic and/or nonionic detergent in the liquid cleaning composition. However, the foaming property of these detergent compositions is not discussed therein.
- U.S. Patent No. 4,129,515 discloses a heavy duty liquid detergent for laundering fabrics comprising a mixture of substantially equal amounts of anionic and nonionic surfactants alkanolamines and magnesium salts, and, optionally, zwitterionic surfactants as suds modifiers.
- U.S. Patent No. 4,224,195 discloses an aqueous detergent composition for laundering socks or stockings comprising a specific group of nonionic detergents, namely, an ethylene oxide of a secondary alcohol, a specific group of anionic detergents, namely, a sulfuric ester salt of an ethylene oxide adduct of a secondary alcohol, and an amphoteric surfactant which may be a betaine, wherein either the anionic or nonionic surfactant may be the major ingredient. The specific class of anionics utilized in this patent is the very same group of anionic detergents expressly excluded in present invention in order to eliminate the alkanol ethoxylate sulfation process and the potential dioxane toxicity problem. Furthermore, this patent finds heavily foaming detergents undesirable for the purpose of washing socks.

The prior art also discloses detergent compositions containing all nonionic surfactants as shown in U.S. Patent Nos. 4,154,706 and 4,329,336 wherein the shampoo compositions contain a plurality of particular nonionic surfactants in order to effect desirable foaming and detersive properties despite the fact that nonionic surfactants are usually deficient in such properties.

10

15

20

25

- U.S. Patent No. 4,013,787 discloses a piperazine based polymer in conditioning and shampoo compositions which may contain all nonionic surfactant or all anionic surfactant.
- U.S. Patent No. 4,450,091 discloses high viscosity shampoo compositions containing a blend of an amphoteric betaine surfactant, a polyoxybutylene polyoxyethylene nonionic detergent, an anionic surfactant, a fatty acid alkanolamide and a polyoxyalkylene glycol fatty ester. But, none of the exemplified compositions contains an active ingredient mixture wherein the nonionic detergent is present in major proportion, probably due to the low foaming properties of the polyoxybutylene polyoxyethylene nonionic detergent.
- U.S. Patent No. 4,595,526 describes a composition comprising a nonionic surfactant, a betaine surfactant, an anionic surfactant and a C<sub>12</sub>-C<sub>14</sub> fatty acid monoethanolamide foam stabilizer.

The Journal of Colloid and Interface Science, Vol. 138, No. 1, August 1990 discloses the synthesis of N-substituted aldonamide and their use in the formation of lyotropic liquid crystals.

Molecular Crystal Liquid Crystal, 1985, Vol. 128, pp. 277-286 and Molecular Crystal Liquid Crystal, 1986, Vol. 135, pp. 93-110 both disclose a new family of liquid crystals which are N-substituted aldonamides.

Belgian Patent No. BE-814,377 teaches preparation of aldonic acid amides and medicaments containing them as analgesic antiinflammatory and vaso dilating agents. However their use as surfactants in a cleaning compositions is not disclosed.

#### Summary of the Invention

The present invention relates to a class of N-alkyl aldonamide surfactants which are used in cleaning compositions in combination with at least one other surfactant which can be a nonionic surfactant, an anionic surfactant, a zwitterionic surfactant, an amine oxide surfactant and an alkyl polyglucoside and mixtures thereof. The resultant cleaning compositions exhibit improved grease and soil removal as well as exhibiting improved mildness.

### <u>Detailed Description of the Invention</u>

5

10

15

25

The present invention relates to a light duty liquid composition comprising by weight:

- (a) 0.5 to 40 wt. %, more preferably 1 to 30 wt. % of at least one first surfactant selected from the group consisting of nonionic surfactants, partially esterified ethoxylated glycerol surfactant, anionic surfactant, and alkylpolyglucoside surfactants and mixtures thereof;
- (b) 0.1 to 10 wt. %, more preferably 0.5 to 8 wt. % of a second surfactant selected from the group consisting sulfonamide, hydroxy sulfobetaine, betaines, amine oxides, glucoamides, N-C<sub>1-3</sub> alkyl C<sub>8</sub>-C<sub>16</sub> alkyl glucoamide, and C<sub>5</sub>-C<sub>12</sub> N-alkyl aldoamide and mixtures thereof;
  - (c) 0 to 12 wt. %, more preferably 0.5 to 8 wt. % of at least one solubilizer; and
  - (d) the balance being water.

The present invention also relates to a light duty liquid microemulsion composition comprising by weight:

- (a) 0.5 to 40 wt. %, more preferably 1 to 30 wt. % of at least one first surfactant selected from the group consisting of nonionic surfactants, partially esterified ethoxylated glycerol surfactant, anionic surfactant, and alkylpolyglucoside surfactants and mixtures thereof;
- (b) 0.1 to 10 wt. %, more preferably 0.5 to 8 wt. % of a second surfactant selected from the group consisting sulfonamide, hydroxy sulfobetaine, betaines, amine oxides, glucoamides, N-C<sub>1-3</sub> alkyl C<sub>8</sub>-C<sub>16</sub> alkyl glucoamide, and C<sub>5</sub>-C<sub>12</sub> N-alkyl aldoamide and mixtures thereof;
  - (c) 0.5 to 50 wt. % of a cosurfactant;
  - (d) 0.4 to 10 wt. % of a perfume, water insoluble hydrocarbon or essential oil;
  - (e) 0 to 12 wt. % of a solubilizer; and
  - (f) the balance being water.

The present invention relates to an all purpose liquid composition comprising by weight:

15

20

- (a) 0.5 to 30 wt. %, more preferably 1 to 25 wt. % of at least one first surfactant selected from the group consisting of nonionic surfactants, partially esterified ethoxylated glycerol surfactant, anionic surfactant, and alkylpolyglucoside surfactants and mixtures thereof;
- (b) 0.1 to 10 wt. %, more preferably 0.5 to 8 wt. % of a second surfactant selected from the group consisting sulfonamide, hydroxy sulfobetaine, betaines, amine oxides, glucoamides, N-C<sub>1-3</sub> alkyl C<sub>8</sub>-C<sub>16</sub> alkyl glucoamide, and C<sub>5</sub>-C<sub>12</sub> N-alkyl aldoamide and mixtures thereof;
  - (c) 0 to 6 wt. % of a solubilizer; and
- 10 (d) the balance being water.

The present invention relates to a microemulsion hard surface cleaning composition comprising by weight:

- (a) 0.5 to 30 wt. %, more preferably 1 to 25 wt. % of at least one first surfactant selected from the group consisting of nonionic surfactants, partially esterified ethoxylated glycerol surfactant, anionic surfactant, and alkylpolyglucoside surfactants and mixtures thereof;
- (b) 0.1 to 10 wt. %, more preferably 0.5 to 8 wt. % of a second surfactant selected from the group consisting sulfonamide, hydroxy sulfobetaine, betaines, amine oxides, glucoamides, N-C<sub>1-3</sub> alkyl  $C_8$ - $C_{16}$  alkyl glucoamide, and  $C_5$ - $C_{12}$  N-alkyl aldoamide and mixtures thereof;
  - (c) 0.5 to 50 wt. % of a cosurfactant;
- (d) 0.4 to 10 wt. % of a perfume, water insoluble hydrocarbon or essential oil; and
  - (e) the balance being water.

The supplemental surfactant used in the instant cleaning compositions is an alkyl aldonamide which is present at a concentration of 0.1 to 10 wt. %, more preferably 0.5 to 8 wt. %.

The N-alkyl aldonamide is depicted by the formula:

15

25

30

0

CH3(CH2)m-NH-C-(CHOH)pCH2OH

wherein m is 6 to 12, more preferably 7 to 11 and p is 3 to 7, more preferably 3 to 5. A

preferred N-alkyl aldoamide is N-octyl reboamide. The N-alkyl aldonamide is prepared by solubilizing the corresponding aldonolactone in methanol and adding to the solution of lactone an amine. The reaction between the lactone and amine is allowed to proceed for 8 hours at room temperature. The resultant N-alkyl aldonamide precipitates out of solution. The precipitate is filtered and recrystallized twice in methanol.

The sulfoamide is depicted by the formula:

wherein n is 7 to 12 such as N-methyl glucamine sulfoamide of a C<sub>8</sub>-C<sub>13</sub> linear alkyl benzene.

The glucamide is depicted by the formula:

wherein R is a C<sub>10</sub> to C<sub>14</sub> alkyl group, such as coco fatty acid-N-methylglucamide.

The inverse glucamide is depicted by the formula:

wherein R<sub>2</sub> is a C<sub>9</sub> to C<sub>12</sub> group, such as N-methyl-cocoalkyl glucamide.

The hydroxy sulfobetaine (hydroxy sultaine) is depicted by the formula:

15

20

25

30

wherein R is a C<sub>12</sub>-C<sub>14</sub> mixed alkyl group of 70 wt. % C<sub>12</sub>and 30 wt. % of C<sub>14</sub>.

The water-soluble zwitterionic surfactant, which can be used in the cleaning compositions is a water soluble betaine having the general formula:

wherein X<sup>-</sup> is selected from the group consisting of CO<sub>2</sub><sup>-</sup> and SO<sub>3</sub><sup>-</sup> and R<sub>1</sub> is an alkyl group having 10 to 20 carbon atoms, preferably 12 to 16 carbon atoms, or the amido radical:

wherein R is an alkyl group having 9 to 19 carbon atoms and a is the integer 1 to 4; R<sub>2</sub> and R<sub>3</sub> are each alkyl groups having 1 to 3 carbons and preferably 1 carbon; R<sub>4</sub> is an alkylene or hydroxyalkylene group having from 1 to 4 carbon atoms and, optionally, one hydroxyl group. Typical alkyldimethyl betaines include decyl dimethyl betaine or 2-(N-decyl-N, N-dimethyl-ammonia) acetate, coco dimethyl betaine or 2-(N-coco N, N-dimethylammonia) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, lauryl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine, etc. The amidobetaines similarly include cocoamidoethylbetaine, cocoamidopropyl betaine and the like. A preferred betaine is coco (C<sub>8</sub>-C<sub>18</sub>) amidopropyl dimethyl betaine. Three preferred betaine surfactants are Genagen CAB and Rewoteric AMB 13 and Golmschmidt Betaine L7.

Another zwitterionic surfactant which can be used in the instant composition is a cocoamido-propylhydroxy sultaine. The sultaine can be depicted by the formula:

wherein R<sub>1</sub> is a saturated or unsaturated alkyl group having 6 to 24 carbon atoms, R<sub>2</sub> is a methyl or ethyl group, R<sub>3</sub> is a methyl or ethyl group, k is 1 to 6, and M<sup>+</sup> is an alkali metal cation. The most preferred hydroxysultaine is a potassium salt of cocoamidopropyl hydroxysultaine.

Amine oxide semi-polar nonionic surfactants which can be used in the instant compositions comprise compounds and mixtures of compounds having the formula:

$$\begin{array}{c} R_2 \\ | \\ R_1(C_2H_4O)_h \ N \rightarrow O \\ | \\ R_3 \end{array}$$

5

10

15

20

25

30

35

wherein  $R_1$  is an alkyl, 2-hydroxyalkyl, 3-hydroxyalkyl, or 3-alkoxy-2-hydroxypropyl radical in which the alkyl and alkoxy, respectively, contain from 8 to 18 carbon atoms,  $R_2$  and  $R_3$  are each methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, or 3-hydroxypropyl, and h is from 0 to 10. Particularly preferred are amine oxides of the formula:

$$\begin{array}{c}
R_2 \\
| \\
R_1 - N \rightarrow 0 \\
| \\
R_3
\end{array}$$

wherein  $R_1$  is a  $C_{12-16}$  alkyl, or cocoamidopropyl group and  $R_2$  and  $R_3$  are methyl or ethyl. The above ethylene oxide condensates, amides, and amine oxides are more fully described in U.S. Pat. No. 4,316,824 which is hereby incorporated herein by reference. Preferred amine oxides are lauryl amine oxide and cocoamido propyl amine oxide.

The water soluble nonionic surfactants utilized in this invention are commercially well known and include the primary aliphatic alcohol ethoxylates, secondary aliphatic alcohol ethoxylates, alkylphenol ethoxylates and ethylene-oxide-propylene oxide condensates on primary alkanols, such a Plurafacs (BASF) and condensates of ethylene

10

15

20

25

12

oxide with sorbitan fatty acid esters such as the Tweens (ICI). The nonionic synthetic organic detergents generally are the condensation products of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic ethylene oxide groups. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a water-soluble nonionic detergent. Further, the length of the polyethenoxy chain can be adjusted to achieve the desired balance between the hydrophobic and hydrophilic elements.

The nonionic surfactant class includes the condensation products of a higher alcohol (e.g., an alkanol containing 8 to 18 carbon atoms in a straight or branched chain configuration) condensed with 5 to 30 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with 16 moles of ethylene oxide (EO), tridecanol condensed with 6 to moles of EO, myristyl alcohol condensed with 10 moles of EO per mole of myristyl alcohol, the condensation product of EO with a cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms in length and wherein the condensate contains either 6 moles of EO per mole of total alcohol or 9 moles of EO per mole of alcohol and tallow alcohol ethoxylates containing 6 EO to 11 EO per mole of alcohol.

A preferred group of the foregoing nonionic surfactants are the Neodol ethoxylates (Shell Co.), which are higher aliphatic, primary alcohol containing 9-15 carbon atoms, such as C9-C<sub>11</sub> alkanol condensed with 8 moles of ethylene oxide (Neodol 91-8), C<sub>12-13</sub> alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C<sub>12-15</sub> alkanol condensed with 12 moles ethylene oxide (Neodol 25-12), C<sub>14-15</sub> alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), and the like. Such ethoxamers have an HLB (hydrophobic lipophilic balance) value of 8-15 and give good O/W emulsification, whereas ethoxamers with HLB values below 8 contain less than 5 ethyleneoxide groups and tend to be poor emulsifiers and poor surfactants.

Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in

10

15

20

25

PCT/US98/08754

a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available nonionic detergents of the foregoing type are C<sub>11</sub>-C<sub>15</sub> secondary alkanol condensed with either 9 EO (Tergitol 15-S-9) or 12 EO (Tergitol 15-S-12) marketed by Union Carbide.

Other suitable nonionic surfactants include the polyethylene oxide condensates of one mole of alkyl phenol containing from 8 to 18 carbon atoms in a straight- or branched chain alkyl group with 5 to 30 moles of ethylene oxide. Specific examples of alkyl phenol ethoxylates include nonyl phenol condensed with 9.5 moles of EO per mole of nonyl phenol, dinonyl phenol condensed with 12 moles of EO per mole of dinonyl phenol, dinonyl phenol condensed with 15 moles of EO per mole of phenol and di-isoctylphenol condensed with 15 moles of EO per mole of phenol and di-isoctylphenol condensed with 15 moles of EO per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630 (nonyl phenol ethoxylate) marketed by GAF Corporation.

Condensates of 2 to 30 moles of ethylene oxide with sorbitan mono- and tri-C<sub>10</sub>-C<sub>20</sub> alkanoic acid esters having a HLB of 8 to 15 also may be employed as the nonionic detergent ingredient in the described shampoo. These surfactants are well known and are available from Imperial Chemical Industries under the Tween trade name. Suitable surfactants include polyoxyethylene (4) sorbitan monolaurate, polyoxyethylene (4) sorbitan monostearate, polyoxyethylene (20) sorbitan tristearate.

The anionic surfactants which may be used in the cleaning compositions of this invention are water soluble such as triethanolamine and include the sodium, potassium, ammonium and ethanolammonium salts of  $C_8$ - $C_{18}$  alkyl sulfates such as lauryl sulfate, myristyl sulfate and the like;  $C_8$ - $C_{18}$  alkyl ethoxylated ether sulfates having 3 to 20 ethylene oxide groups; linear  $C_8$ - $C_{16}$  alkyl benzene sulfonates;  $C_{10}$ - $C_{20}$  paraffin sulfonates; alpha olefin sulfonates containing 10-24 carbon atoms;  $C_8$ - $C_{18}$  alkyl sulfoacetates;  $C_8$ - $C_{18}$  alkyl sulfosuccinate esters;  $C_8$ - $C_{18}$  acyl isethionates; and  $C_8$ - $C_{18}$  acyl taurates. Preferred anionic surfactants are the water soluble  $C_{12}$ - $C_{16}$  alkyl sulfates, the  $C_{10}$ - $C_{15}$  alkylbenzene sulfonates, the  $C_{13}$ - $C_{17}$  paraffin sulfonates and the alpha  $C_{12}$ - $C_{18}$  olefin sulfonates.

The instant composition can contain a surfactant (herein after referred to as ethoxylated glycerol type compound) which is a mixture of a fully esterified ethoxylated polyhydric alcohol, a partially esterified ethoxylated polyhydric alcohol and a nonesterified ethoxylated polyhydric alcohol is glycerol, and the compound is

 $\begin{array}{c} R' \\ CH_2O(CH_2CHO)_{\overline{X}}B \\ \mid R' \\ [CHO(CH_2CHO)_{\overline{Y}}B]_{\overline{W}} \\ \mid R' \\ \mid R' \\ \mid CH_2O(CH_2CHO)_{\overline{Z}}B \end{array}$  Formula

and

5

10

15

$$\begin{array}{c} R' \\ \text{CH}_2\text{O}(\text{CH}_2\text{CHO})_{\overline{X}} + H \\ R' \\ \text{CHO}(\text{CH}_2\text{CHO})_{\overline{Y}} + H \\ R' \\ R' \\ \text{CH}_2\text{O}(\text{CH}_2\text{CHO})_{\overline{Z}} + H \end{array}$$
 Formula

wherein w equals one to four, most preferably one. B is selected from the group consisting of hydrogen or a group represented by:

wherein R is selected from the group consisting of alkyl group having 6 to 22 carbon atoms, more preferably 11 to 15 carbon atoms and alkenyl groups having 6 to 22 carbon atoms, more preferably 11 to 15 carbon atoms, wherein a hydrogenated tallow alkyl chain or a coco alkyl chain is most preferred, wherein at least one of the B groups is represented by said

O || P

5

10

15

20

25

and R' is selected from the group consisting of hydrogen and methyl groups; x, y and z have a value between 0 and 60, more preferably 0 to 40, provided that (x+y+z) equals 2 to 100, preferably 4 to 24 and most preferably 4 to 19, wherein in Formula (I) the ratio of monoester / diester / triester is 45 to 90 / 5 to 40 / 1 to 20, more preferably 50 to 90 / 9 to 32 / 1 to 12, wherein the ratio of Formula (I) to Formula (II) is a value between 3 to 0.02, preferably 3 to 0.1, most preferably 1.5 to 0.2, wherein it is most preferred that there is more of Formula (II) than Formula (I) in the mixture that forms the compound.

The ethoxylated glycerol type compound used in the instant composition is manufactured by the Kao Corporation and sold under the trade name Levenol such as Levenol F-200 which has an average EO of 6 and a molar ratio of coco fatty acid to glycerol of 0.55 or Levenol V501/2 which has an average EO of 17 and a molar ratio of tallow fatty acid to glycerol of 1.0. It is preferred that the molar ratio of the fatty acid to glycerol is less than 1.7, more preferably less than 1.5 and most preferably less than 1.0. The ethoxylated glycerol type compound has a molecular weight of 400 to 1600, and a pH (50 grams / liter of water) of 5-7. The Levenol compounds are substantially non irritant to human skin and have a primary biodegradabillity higher than 90% as measured by the Wickbold method Bias-7d.

Two examples of the Levenol compounds are Levenol V-501/2 which has 17 ethoxylated groups and is derived from tallow fatty acid with a fatty acid to glycerol ratio of 1.0 and a molecular weight of 1465 and Levenol F-200 has 6 ethoxylated groups and is derived from coco fatty acid with a fatty acid to glycerol ratio of 0.55. Both Levenol F-200 and Levenol V-501/2 are composed of a mixture of Formula (I) and Formula (II). The Levenol compounds has ecoxicity values of algae growth inhibition > 100 mg/liter; acute toxicity for Daphniae > 100 mg/liter and acute fish toxicity > 100 mg/liter. The Levenol compounds have a ready biodegradability higher than 60% which is the minimum required value according to OECD 301B measurement to be acceptably biodegradable.

10

15

20

25

WO 98/50508 PCT/US98/08754

Polyesterified nonionic compounds also useful in the instant compositions are Crovol PK-40 and Crovol PK-70 manufactured by Croda GMBH of the Netherlands. Crovol PK-40 is a polyoxyethylene (12) Palm Kernel Glyceride which has 12 EO groups. Crovol PK-70 which is prefered is a polyoxyethylene (45) Palm Kernel Glyceride have 45 EO groups.

The instant compositions can contain an alkyl polysaccharide surfactant. The alkyl polysaccharides surfactants, which are used in conjunction with the aforementioned surfactant have a hydrophobic group containing from 8 to 20 carbon atoms, preferably from 10 to 16 carbon atoms, most preferably from 12 to 14 carbon atoms, and polysaccharide hydrophilic group containing from 1.5 to 10, preferably from 1.5 to 4, most preferably from 1.6 to 2.7 saccharide units (e.g., galactoside, glucoside, fructoside, glucosyl, fructosyl; and/or galactosyl units). Mixtures of saccharide moieties may be used in the alkyl polysaccharide surfactants. The number x indicates the number of saccharide units in a particular alkyl polysaccharide surfactant. For a particular alkyl polysaccharide molecule x can only assume integral values. In any physical sample of alkyl polysaccharide surfactants there will be in general molecules having different x values. The physical sample can be characterized by the average value of x and this average value can assume non-integral values. In this specification the values of x are to be understood to be average values. The hydrophobic group (R) can be attached at the 2-, 3-, or 4- positions rather than at the 1-position, (thus giving e.g. a glucosyl or galactosyl as opposed to a glucoside or galactoside). However, attachment through the 1- position, i.e., glucosides. galactoside, fructosides, etc., is preferred. In the preferred product the additional saccharide units are predominately attached to the previous saccharide unit's 2-position. Attachment through the 3-, 4-, and 6- positions can also occur. Optionally and less desirably there can be a polyalkoxide chain joining the hydrophobic moiety (R) and the polysaccharide chain. The preferred alkoxide moiety is ethoxide.

Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from 8 to 20, preferably from 10 to 18 carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can

10

15

20

25

PCT/US98/08754

contain up to 3 hydroxy groups and/or the polyalkoxide chain can contain up to 30, preferably less than 10, alkoxide moieties.

Suitable alkyl polysaccharides are decyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexaglucosides, galactosides. lactosides, fructosides, fructosyls, lactosyls, glucosyls and/or galactosyls and mixtures thereof.

The alkyl monosaccharides are relatively less soluble in water than the higher alkyl polysaccharides. When used in admixture with alkyl polysaccharides, the alkyl monosaccharides are solubilized to some extent. The use of alkyl monosaccharides in admixture with alkyl polysaccharides is a preferred mode of carrying out the invention. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentaglucosides and tallow alkyl tetra-, penta-, and hexaglucosides.

The preferred alkyl polysaccharides are alkyl polyglucosides having the formula  $R_2O(C_nH_{2n}O)r(Z)_X$ 

wherein Z is derived from glucose, R is a hydrophobic group selected from the group consisting of alkyl, alkylphenyl, hydroxyalkylphenyl, and mixtures thereof in which said alkyl groups contain from 10 to 18, preferably from 12 to 14 carbon atoms; n is 2 or 3 preferably 2, r is from 0 to 10, preferable 0; and x is from 1.5 to 8, preferably from 1.5 to 4. most preferably from 1.6 to 2.7. To prepare these compounds a long chain alcohol (R2OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkyl polyglucosides can be prepared by a two step procedure in which a short chain alcohol (R<sub>1</sub>OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkyl polyglucosides can be prepared by a two step procedure in which a short chain alcohol (C1-6) is reacted with glucose or a polyglucoside (x=2 to 4) to yield a short chain alkyl glucoside (x=1 to 4) which can in turn be reacted with a longer chain alcohol (R2OH) to displace the short chain alcohol and obtain the desired alkyl polyglucoside. If this two step procedure is used, the short chain alkylglucoside content of the final alkyl polyglucoside material should be less

10

15

20

25

than 50%, preferably less than 10%, more preferably less than 5%, most preferably 0% of the alkyl polyglucoside.

The amount of unreacted alcohol (the free fatty alcohol content) in the desired alkyl polysaccharide surfactant is preferably less than 2%, more preferably less than 0.5% by weight of the total of the alkyl polysaccharide. For some uses it is desirable to have the alkyl monosaccharide content less than 10%.

The used herein, "alkyl polysaccharide surfactant" is intended to represent both the preferred glucose and galactose derived surfactants and the less preferred alkyl polysaccharide surfactants. Throughout this specification, "alkyl polyglucoside" is used to include alkyl polyglycosides because the stereochemistry of the saccharide moiety is changed during the preparation reaction.

An especially preferred APG glycoside surfactant is APG 625 glycoside manufactured by the Henkel Corporation of Ambler, PA. APG25 is a nonionic alkyl polyglycoside characterized by the formula:

#### $C_nH_{2n+1}O(C_6H_{10}O_5)_xH$

wherein n=10 (2%); n=122 (65%); n=14 (21-28%); n=16 (4-8%) and n=18 (0.5%) and x (degree of polymerization) = 1.6. APG 625 has: a pH of 6 to 10 (10% of APG 625 in distilled water); a specific gravity at 25°C of 1.1 g/ml; a density at 25°C of 9.1 lbs/gallon; a calculated HLB of 12.1 and a Brookfield viscosity at 35°C, 21 spindle, 5-10 RPM of 3,000 to 7,000 cps.

A water insoluble saturated or unsaturated organic compound can be optionally used. The water insoluble saturated or unsaturated organic compound is selected from the group consisting of perfumes, essential oils or water insoluble hydrocarbons containing a cycloalkyl group having 5 to 10 carbon atoms, wherein the alkyl or cycloalkyl group can be saturated or unsaturated and the cycloalkyl group can have one or more saturated or unsaturated alkyl groups having 1 to 20 carbon atoms affixed to the alkyl or cycloalkyl group and one or more halogens, alcohols, nitro or ester group substituted on the cycloalkyl group or alkyl group; aromatic hydrocarbons; water insoluble ethers; water insoluble carboxylic acids, water insoluble alcohols, water insoluble amines, water

10

WO 98/50508 PCT/US98/08754 19

insoluble aromatic or aliphatic esters, nitropropane, 2,5dimethylhydrofuran, 2-ethyl2-methyl 1,3dioxolane, 3-ethyl 4-propyl tetrahydropyran, N-isopropyl morpholine, alpha-methyl benzyldimethylamine, methyl chloraform and methyl perchlorapropane, and mixtures thereof. Typical hydrocarbons are cyclohexyl-1decane, methyl-3 cyclohexyl-9 nonane. methyl-3 cyclohexyl-6 nononane, dimethyl cycloheplane, trimethyl cyclopentane, ethyl-2 isopropyl-4 cyclohexane. Typical aromatic hydrocarbons are bromotoluene, diethyl benzene, cyclohexyl bromoxylene, ethyl-3 pentyl-4 toluene, tetrahydronaphthalene. nitrobenzene, and methyl naphthalene. Typical water insoluble esters are benzyl acetate. dicyclopentadienylacetate, isononyl acetate, isobornyl acetate and isobutyl isobutyrate. Typical water insoluble ethers are di(alphamethyl benzyl) ether, and diphenyl ether. A typical alcohol is phenoxyethanol. A typical water insoluble nitro derivative is nitro propane.

Suitable essential oils are selected from the group consisting of: Anethole 20/21 natural, Aniseed oil china star, Aniseed oil globe brand, Balsam (Peru). 15 Basil oil (India), Black pepper oil, Black pepper oleoresin 40/20, Bois de Rose (Brazil) FOB. Borneol Flakes (China), Camphor oil, White, Camphor powder synthetic technical. Cananga oil (Java), Cardamom oil, Cassia oil (China), Cedarwood oil (China) BP, Cinnamon bark oil, Cinnamon leaf oil, Citronella oil, Clove bud oil, Clove leaf, Corjander (Russia), Coumarin 69°C (China), Cyclamen Aldehyde, Diphenyl oxide, Ethyl vanilin. 20 Eucalyptol, Eucalyptus oil, Eucalyptus citriodora, Fennel oil, Geranium oil, Ginger oil, Ginger oleoresin (India), White grapefruit oil, Guaiacwood oil, Gurjun balsam, Heliotropin. Isobornyl acetate, Isolongifolene, Juniper berry oil, L-methyl acetate, Lavender oil, Lemon oil, Lemongrass oil, Lime oil distilled, Litsea Cubeba oil, Longifolene, Menthol crystals. Methyl cedryl ketone, Methyl chavicol, Methyl salicylate, Musk ambrette, Musk ketone. 25 Musk xylol, Nutmeg oil, Orange oil, Patchouli oil, Peppermint oil, Phenyl ethyl alcohol. Pimento berry oil, Pimento leaf oil, Rosalin, Sandalwood oil, Sandenol, Sage oil, Clary sage, Sassafras oil, Spearmint oil, Spike lavender, Tagetes, Tea tree oil, Vanilin, Vetyver oil (Java), Wintergreen, Allocimene, Arbanex<sup>TM</sup>, Arbanol<sup>®</sup>, Bergamot oils, Camphene, Alpha-Campholenic aldehyde, I-Carvone, Cineoles, Citral, Citronellol Terpenes, Alpha-

10

15

20

25

PCT/US98/08754

Citronellol, Citronellyl Acetate, Citronellyl Nitrile, Para-Cymene, Dihydroanethole, Dihydrocarveol, d-Dihydrocarvone, Dihydrolinalool, Dihydromyrcene, Dihydromyrcenol, Dihydromyrcenyl Acetate, Dihydroterpineol, Dimethyloctanal, Dimethyloctanol, Dimethyloctanyl Acetate, Estragole, Ethyl-2 Methylbutyrate, Fenchol, Ferniol<sup>TM</sup>, Florilys<sup>TM</sup>. Geraniol, Geranyl Acetate, Geranyl Nitrile, Glidmint<sup>TM</sup> Mint oils, Glidox<sup>TM</sup>, Grapefruit oils, trans-2-Hexenal, trans-2-Hexenol, cis-3-Hexenyl Isovalerate, cis-3-Hexanyl-2methylbutyrate, Hexyl Isovalerate, Hexyl-2-methylbutyrate, Hydroxycitronellal, Ionone, Isobornyl Methylether, Linalool, Linalool Oxide, Linalyl Acetate, Menthane Hydroperoxide. I-Methyl Acetate, Methyl Hexyl Ether, Methyl-2-methylbutyrate, 2-Methylbutyl Isovalerate. Myrcene, Nerol, Neryl Acetate, 3-Octanol, 3-Octyl Acetate, Phenyl Ethyl-2-methylbutyrate, Petitgrain oil, cis-Pinane, Pinane Hydroperoxide, Pinanol, Pine Ester, Pine Needle oils, Pine oil, alpha-Pinene, beta-Pinene, alpha-Pinene Oxide, Plinol, Plinyl Acetate, Pseudo Ionone, Rhodinol, Rhodinyl Acetate, Spice oils, alpha-Terpinene, gamma-Terpinene. Terpinene-4-OL, Terpineol, Terpinolene, Terpinyl Acetate, Tetrahydrolinalool, Tetrahydrolinalyl Acetate, Tetrahydromyrcenol, Tetralol®, Tomato oils, Vitalizair. Zestoral<sup>TM</sup>.

The cosurfactant may play an essential role in the formation of the microemulsion and the concentrated microemulsion compositions of the instant invention. Very briefly, in the absence of the cosurfactant the water, detergent(s) and hydrocarbon (e.g., perfume) will, when mixed in appropriate proportions form either a micellar solution (low concentration) or form an oil-in-water emulsion in the first aspect of the invention. With the cosurfactant added to this system, the interfacial tension at the interface between the emulsion droplets and aqueous phase is reduced to a very low value. This reduction of the interfacial tension results in spontaneous break-up of the emulsion droplets to consecutively smaller aggregates until the state of a transparent colloidal sized emulsion. e.g., a microemulsion, is formed. In the state of a microemulsion, thermodynamic factors come into balance with varying degrees of stability related to the total free energy of the microemulsion. Some of the thermodynamic factors involved in determining the total free energy of the system are (1) particle-particle potential; (2) interfacial tension or free energy

10

15

20

25

(stretching and bending); (3) droplet dispersion entropy; and (4) chemical potential changes upon formation. A thermodynamically stable system is achieved when (2) interfacial tension or free energy is minimized and (3) droplet dispersion entropy is maximized.

Thus, the role of cosurfactant in formation of a stable o/w microemulsion is to (a) decrease interfacial tension (2); and (b) modify the microemulsion structure and increase the number of possible configurations (3). Also, the cosurfactant will (c) decrease the rigidity. Generally, an increase in cosurfactant concentration results in a wider temperature range of the stability of the product.

The major class of compounds found to provide highly suitable cosurfactants for the microemulsion over temperature ranges extending from 5°C to 43°C for instance are water-soluble polyethylene glycols having a molecular weight of 150 to 1000, polypropylene glycol of the formula HO(CH3CHCH2O)<sub>n</sub>H wherein n is a number from 2 to 18, mixtures of polyethylene glycol and polypropyl glycol (Synalox) and mono and di C1-C6 alkyl ethers and esters of ethylene glycol and propylene glycol having the structural formulas R(X)<sub>n</sub>OH R<sub>1</sub>(X)<sub>n</sub>OH R(X)<sub>n</sub>OR and R<sub>1</sub>(X)<sub>n</sub>OR<sub>1</sub>wherein R is C1-C6 alkyl group, R<sub>1</sub> is C2-C4 acyl group, X is (OCH<sub>2</sub>CH<sub>2</sub>) or (OCH<sub>2</sub>(CH<sub>3</sub>)CH) and n is a number from 1 to 4, diethylene glycol, triethylene glycol, an alkyl lactate, wherein the alkyl group has 1 to 6 carbon atoms, 1methoxy-2-propanol, 1methoxy-3-propanol, and 1methoxy 2-, 3- or 4-butanol.

Representative members of the polypropylene glycol include dipropylene glycol and polypropylene glycol having a molecular weight of 150 to 1000, e.g., polypropylene glycol 400. Other satisfactory glycol ethers are ethylene glycol monobutyl ether (butyl cellosolve), diethylene glycol monobutyl ether (butyl carbitol), triethylene glycol monobutyl ether, mono, di, tri propylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, mono, di, tripropylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, propylene glycol tertiary butyl ether, ethylene glycol monomethyl ether, diethylene glycol monomethyl ether,

10

15

20

25

diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, diethylene glycol monopentyl ether, triethylene glycol monomethyl ether, triethylene glycol monopentyl ether, mono, di tripropylene glycol monopentyl ether, mono, di, tripropylene glycol monopentyl ether, mono, di, tripropylene glycol monomethyl ether, mono, di, tributylene glycol monomethyl ether, mono, di, tributylene glycol monopentyl ether, mono, di, tributylene glycol monopentyl ether, mono, di, tributylene glycol monopentyl ether and mono, di, tributylene glycol monobetyl ether, ethylene glycol monoacetate and dipropylene glycol propionate. When these glycol type cosurfactants are at a concentration of 1.0 to 50 wt. %, more preferably 1.5 wt. % to 20 wt. %, especially preferably 2 wt. % to 15 wt. % in combination with a water insoluble hydrocarbon at a concentration composition.

PCT/US98/08754

While all of the aforementioned glycol ether compounds provide the described stability, the most preferred cosurfactant compounds of each type, on the basis of cost and cosmetic appearance (particularly odor), are dipropylene glycol monomethyl ether and diethylene glycol monobutyl ether. Other suitable water insoluble cosurfactants are water soluble esters such as ethyl lactate and water soluble carbohydrates such as butyl glycosides.

The amount of cosurfactant required to stabilize the microemulsion compositions will, of course, depend on such factors as the surface tension characteristics of the cosurfactant, the type and amounts of the primary surfactants and water insoluble hydrocarbon, and the type and amounts of any other additional ingredients which may be present in the composition and which have an influence on the thermodynamic factors enumerated above. Generally, amounts of cosurfactant in the range of from 0 to 50 wt. %, preferably from 1 wt. % to 20 wt. %, more preferably from 2 wt. % to 15 wt. % provide stable dilute o/w microemulsions for the above-described levels of primary surfactants and water insoluble hydrocarbon and any other additional ingredients as described below.

10

15

20

25

PCT/US98/08754

The ability to formulate mild, acid or neutral products without builders which have grease removal capacities is a feature of the present invention because the prior art o/w microemulsion formulations most usually are highly alkaline or highly built or both.

The instant microemulsion formulas explicitly exclude alkali metal silicates and alkali metal builders such as alkali metal polyphosphates, alkali metal carbonates, alkali metal phosphonates and alkali metal citrates because these materials, if used in the instant composition, would cause the composition to have a high pH as well as leaving residue on the surface being cleaned.

The surfactants discussed above can be solubilized in one prefered nonmicroemulsion embodiment of the invention in an aqueous medium comprising water and a mixture of an alkyl monoethanol amides such as C<sub>12</sub>-C<sub>14</sub> alkyl monoethanol amide (LMMEA) at a concentration of 1 to 4 wt. %, and an alkyl diethanol amides such as coco diethanol amide (CDEA) or lauryl diethanol amide (LDEA) at a concentration of 1 to 4 wt. % wherein the ratio of monoethanol amide to diethanol amide is 3:1 to 1:3.

Less preferred solubilizing agents are C2-C3 mono and di-hydroxy alkanols, e.g., ethanol, isopropanol and propylene glycol. Suitable water soluble hydrotropic salts include sodium, potassium, ammonium and mono-, di- and triethanolammonium salts. While the aqueous medium is primarily water, preferably said solubilizing agents are included in order to control the viscosity of the liquid composition and to control low temperature cloud clear properties. Usually, it is desirable to maintain clarity to a temperature in the range of 5°C to 10°C. Therefore, the proportion of solubilizer generally will be from 1% to 15%. preferably 2% to 12%, most preferably 3%-8%, by weight of the detergent composition with the proportion of ethanol, when present, being 5% of weight or less in order to provide a composition having a flash point above 46°C. Preferably the solubilizing ingredient will be a mixture of ethanol and a water soluble salt of a C1-C3 substituted benzene sulfonate hydrotrope such as sodium xylene sulfonate or sodium cumene sulfonate or a mixture of said sulfonates or ethanol and urea. Inorganic alkali metal or alkaline earth metal salts such as sodium sulfate, magnesium sulfate, sodium chloride and sodium citrate can be added at concentrations of 0.5 to 4.0 wt.% to modify the cloud point of the nonionic

10

15

20

surfactant and thereby control the haze of the resultant solution. Various other ingredients such as urea at a concentration of 0.5 to 4.0 wt.% or urea at the same concentration in combination with ethanol at a concentration of 0.5 to 4.0 wt.% can be used as solubilizing agents.

The cleaning composition of this invention may, if desired, also contain other components either to provide additional effect or to make the product more attractive to the consumer. The following are mentioned by way of example: Colors or dyes in amounts up to 0.5% by weight; bactericides in amounts up to 1% by weight; preservatives or antioxidizing agents, such as formalin, 5-bromo-5-nitro-dioxan-1,3; 5-chloro-2-methyl-4-isothaliazolin-3-one, 2,6-di-tert.butyl-p-cresol, etc., in amounts up to 2% by weight; and pH adjusting agents, such as sulfuric acid or sodium hydroxide, as needed. Furthermore, if opaque compositions are desired, up to 4% by weight of an opacifier may be added.

The final ingredient in the instant composition is water. The instant cleaning compositions are made by simple mixing at temperatures of 25°C to 50°C.

The following example illustrates liquid cleaning compositions of the described invention. Unless otherwise specified, all percentages are by weight. The exemplified compositions are illustrative only and do not limit the scope of the invention. Unless otherwise specified, the proportions in the examples and elsewhere in the specification are by weight.

After Example, cleaning compositons A through E are optically clear, in a single phase, and stable at 4°C.

Example 1

The following compositions in wt. % were prepared by simple mixing procedure:

Raw Materials	Α	В	С	D	Е	Н	G
Sodium paraffin sulfonate C <sub>14</sub> -C <sub>17</sub> (60%)					4.7		25.5
Sodium C9-C <sub>13</sub> linear alkylbenzene	5.95	6.12	5.95	2.98			
sulfonate (52%)			1				
Magnesium Cg-C <sub>13</sub> linear alkylbenzene				2.98			
sulfonate (43.7%)		ŀ					
NaAEOS (1.3:1) (59%)						18.5	
NaAEOS (2:1) (70%)							8.5
N-octyl ribonamide (98%)	1.05	1.35		1.05	1.0	2.0	2.0
N-decyl ribonamide (98%)			1.05				-
Levenol F-200		1.53			2.3		
Neodol 1.9 (C <sub>10</sub> E9)						8.5	
APG 625 (50.5%)						6.8	
C <sub>12</sub> -C <sub>14</sub> alkyl dimethyl betaine (30%)						3.0	
Cocoamido propyl amine oxide (35%)						4.0	
Diethylene glycol mono n-butyl ether	2.0		8.0	6.0	5.5		
Dipropylene glycol mono methyl ether							8.0
Urea							5.0
Coco Fatty Acid				0.75	0.75		
MgSO <sub>4</sub> ·7H <sub>2</sub> O					2.2	3.5	
NaOH (50%)				0.11	0.07		
d-Limonene							6.0
Perfume	0.8		0.8	0.8	0.8		0.5
Minors				0.2	0.2		0.2
Water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Physical stability		<u> </u>	<u> </u>				
RT	Yes	Yes	Yes	Yes	Yes	Yes	Yes
4°C (one week)	Yes	Yes	Yes	Yes	Yes	Hazy	Yes

### Example 2

## 5 The following compositions in wt. % were prepared:

Raw Materials	Α	В	С	D	E	F	G	Н
Sodium lauryl sulfate (99%)	1.0		0.4	0.4	0.05	0.4		
Linear alkylbenzene sulfonate (LAS) C9- C13 sodium salt (52%)		0.8					0.4	0.4
Coco (C12-C14) fatty acid-N-methylglucamide (95%)			0.4					
N-methylglucamine sulfonamide of C9-C13 linear alkylbenzene (95%)				0.4				
N-octyl ribonamide (98%)					0.05			
N-methyl-cocoalkylglucamide (98%)						0.4		
Cocoamidopropyl betaine (30%)							0.4	
Cocoamidopropyl hydroxy sulfobetaine (44%)								0.4
Water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Adhesion tension (a)	10.2	13.2	15.5	19.4	10.0	15.7	18.5	18.0
Contact angle (a)	73°	68°	57°	44.5°	72.5°	54.5°	48°	48°

(a) adhesion tension and contact angle measured at a concentration of 1 gram of surfactant per liter of water at 25°C on glycerol tripalmitate.

WO 98/50508

26

PCT/US98/08754

#### What Is Claimed Is

5

- 1. A cleaning composition comprising by weight:
- (a) 0.5 to 40 wt. % of at least one first surfactant selected from the group consisting of nonionic surfactants, anionic surfactants, partially esterified ethoxylated glycerol surfactants, and alkyl polyglucoside surfactants and mixtures thereof;
- (b) 0.1 to 10% of a second surfactant selected from the group consisting of sulfonamide, hydroxy sulfobetaine, betaines, amine oxides, glucoamides, N-C $_{1-3}$  alkyl C $_{8}$ -C $_{16}$  alkyl glucoamide, and C $_{5}$ -C $_{12}$  N-alkyl aldoamide and mixtures thereof;; and
  - (c) the balance being water.
- 10 2. The composition of Claim 1 further including 0 to 12% of at least one solubilizer.
  - 3. The composition of Claim 2 further including 0.5 to 50% of a cosurfactant.
  - 4. The composition of Claim 3 further including 0.4 to 10% of a perfume, water insoluble organic compound or essential oil.
- 15 5. The composition of Claim 1 wherein the concentration of the at least one surfactant is 0.5 to 30%.
  - 6. The composition of Claim 5 further including 0 to 6% of a solubilizer.
  - 7. The composition of Claim 5 further including 0.5 to 50% of a cosurfactant.
- 8. The composition of Claim 7 further including 0.4 to 10% of a perfume, water insoluble organic compound or essential oil.

Intern. Junal Application No PCT/US 98/08754

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C11D1/94 C11D1/86 C11D17/00

/86 C11D1/65

C11D1/825

C11D1/83

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WO 98 10048 A (COLGATE-PALMOLIVE COMPANY) 12 March 1998 see examples	1-8
see the whole document	
WO 94 12511 A (UNILEVER PLC) 9 June 1994 see page 8 - page 17 see examples	1
EP 0 796 842 A (UNILEVER PLC) 24 September 1997 see examples 18,19	1,2,4-6,
US 5 523 025 A (R. ERILLI) 4 June 1996 see column 8, line 19 - line 54 see examples H-K,O,R,S,U,V	1-8
	see page 8 - page 17 see examples  EP 0 796 842 A (UNILEVER PLC) 24 September 1997 see examples 18,19  US 5 523 025 A (R. ERILLI) 4 June 1996 see column 8, line 19 - line 54

X Further documents are listed in the continuation of box C.	χ Patent family members are listed in annex.
"A" document defining the general state of the art which is not considered to be of particular relevance  "E" earlier document but published on or after the international filing date  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  "O" document referring to an oral disclosure, use, exhibition or other means  "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  "8" document member of the same patent family
Date of the actual completion of theinternational search  10 September 1998	Date of mailing of the international search report $22/09/1998$
Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2  NL - 2280 HV Rijswijk  Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  Fax: (+31-70) 340-3016	Authorized officer  Ketterer, M

1

Intern and Application No
PCT/US 98/08754

	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	Relevant to claim No.
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Helevant to claim No.
A	WO 96 15216 A (COLGATE-PALMOLIVE COMPANY) 23 May 1996 see page 18, line 20 - page 19, line 2 see page 22, line 9 - page 34 see examples	1-8
Ą	US 5 415 813 A (A. M. MISSELYN ET. AL.) 16 May 1995 see examples see claims	1-8
X	WO 96 18717 A (COLGATE-PALMOLIVE COMPANY) 20 June 1996 see examples	1
X	WO 96 16160 A (COLGATE-PALMOLIVE COMPANY) 30 May 1996 see examples	1
X	WO 97 04059 A (COLGATE-PALMOLIVE COMPANY) 6 February 1997 see examples	1
Ρ,Χ	WO 98 00506 A (COLGATE-PALMOLIVE COMPANY) 8 January 1998 see examples	1
X	WO 96 26262 A (COLGATE-PALMOLIVE COMPANY) 29 August 1996 see examples	1
l		
!		

1

Information on patent family members

Inter: anal Application No
PCT/US 98/08754

Patent document cited in search report	t	Publication date		atent family nember(s)	Publication date
WO 9810048	Α	12-03-1998	US AU	5665689 A 4239697 A	09-09-1997 26-03-1998
WO 9412511	A	09-06-1994	AU CZ DE DE EP ES HU JP PL SK US	5465594 A 9501345 A 69314347 D 69314347 T 0670844 A 2107788 T 72617 A 8503477 T 309226 A 69095 A 5521293 A	22-06-1994 13-12-1995 06-11-1997 29-01-1998 13-09-1995 01-12-1997 28-05-1996 16-04-1996 02-10-1995 09-08-1995 28-05-1996
EP 796842	Α	24-09-1997	US US CA US	5688996 A 5668098 A 2199352 A 5739093 A	18-11-1997 16-09-1997 19-09-1997 14-04-1998
US 5523025	A	04-06-1996	AU CA EP WO US	4927296 A 2213626 A 0815194 A 9626262 A 5646104 A	11-09-1996 29-08-1996 07-01-1998 29-08-1996 08-07-1997
WO 9615216	A	23-05-1996	US US AU AU BR CA CN CZ EP HU NZ	5486307 A 5573702 A 682739 B 1209295 A 4109696 A 9408123 A 9509676 A 2205399 A 1171132 A 9701503 A 0730635 A 0791045 A 77101 A 277159 A	23-01-1996 12-11-1996 16-10-1997 13-06-1995 06-06-1996 05-08-1997 16-09-1997 23-05-1996 21-01-1998 17-12-1997 11-09-1996 27-08-1997 02-03-1998 26-05-1997

information on patent family members

Inter. unal Application No
PCT/US 98/08754

Patent document cited in search report		Publication date	Pá n	atent family nember(s)	Publication date	
WO S	9615216	Α		PL PL WO	314619 A 320228 A 9514762 A	16-09-1996 15-09-1997 01-06-1995
US !	5415813	A	16-05-1995	AU AU BR EP PL WO US	685204 B 1178795 A 9408120 A 0730634 A 319156 A 9514763 A 5552089 A	15-01-1998 13-06-1995 05-08-1997 11-09-1996 21-07-1997 01-06-1995 03-09-1996
WO	9618717	A	20-06-1996	US US AU CA EP PL	5529723 A 5580848 A 4376496 A 2207683 A 0797657 A 321067 A	25-06-1996 03-12-1996 03-07-1996 20-06-1996 01-10-1997 24-11-1997
WO	9616160	А	30-05-1996	US AU CA EP PL US	5531938 A 4247896 A 2205854 A 0793712 A 320415 A 5741769 A	02-07-1996 17-06-1996 30-05-1996 10-09-1997 29-09-1997 21-04-1998
WO	9704059	Α	06-02-1997	AU EP PL US	6498196 A 0839177 A 324624 A 5770554 A	18-02-1997 06-05-1998 08-06-1998 23-06-1998
WO	9800506	Α	08-01-1998	US AU	5741769 A 3372697 A	21-04-1998 21-01-1998
WO	9626262	A	29-08-1996	US US AU CA EP	5523025 A 5646104 A 4927296 A 2213626 A 0815194 A	04-06-1996 08-07-1997 11-09-1996 29-08-1996 07-01-1998